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Design of Shallow p-type dopants in ZnO

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Introduction

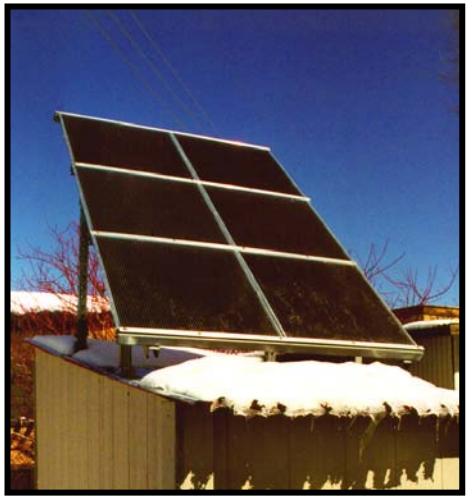
- ZnO is a promising material for short wave-length opto-electronic devices such as UV lasers and LEDs due to its large exciton binding energy and low material cost

- ZnO can be doped easily n-type, but the realization of stable p-type ZnO is rather difficult

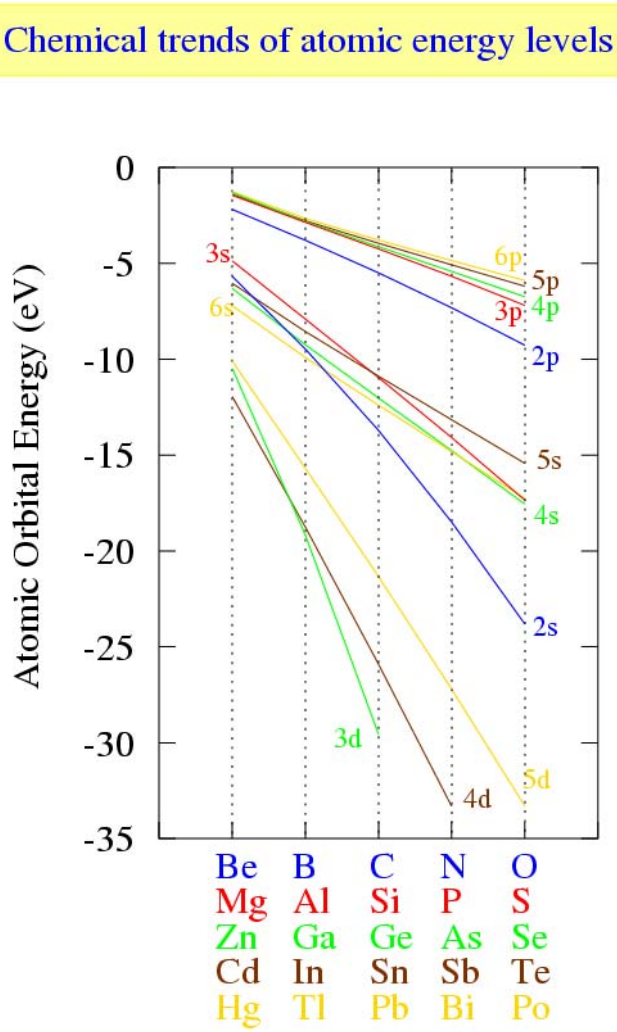
Using first-principles band structure methods we will address:

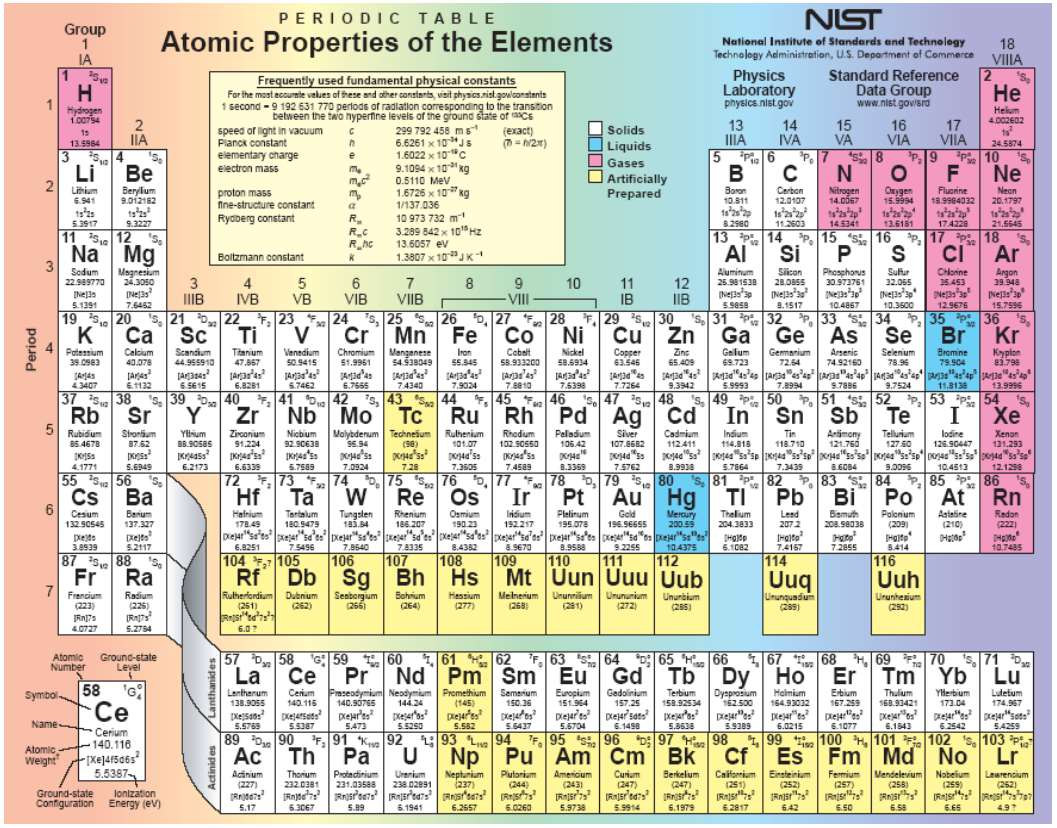
- What causes the p-type doping difficulty in ZnO

- How to overcome the p-type doping difficulty in ZnO



Chemical Trends of Atomic Energy Levels





Atomic potential becomes more negative when the atomic number increases from left to right in the Periodic Table

Method of Calculation

Method of calculation

- Band structure and total energy are calculated using the first-principles band structure method (FLAPW, PP) with local density approximation (LDA)

- Defects are described using the supercell approach. A uniform background charge is added for charged defect calculation

- All the internal structural parameters are optimized by minimizing the quantum mechanical forces

- Band in different supercell calculations are aligned using atomic core levels or average potentials

S.-H. Wei, Computational Materials Science **30**, 337 (2004)

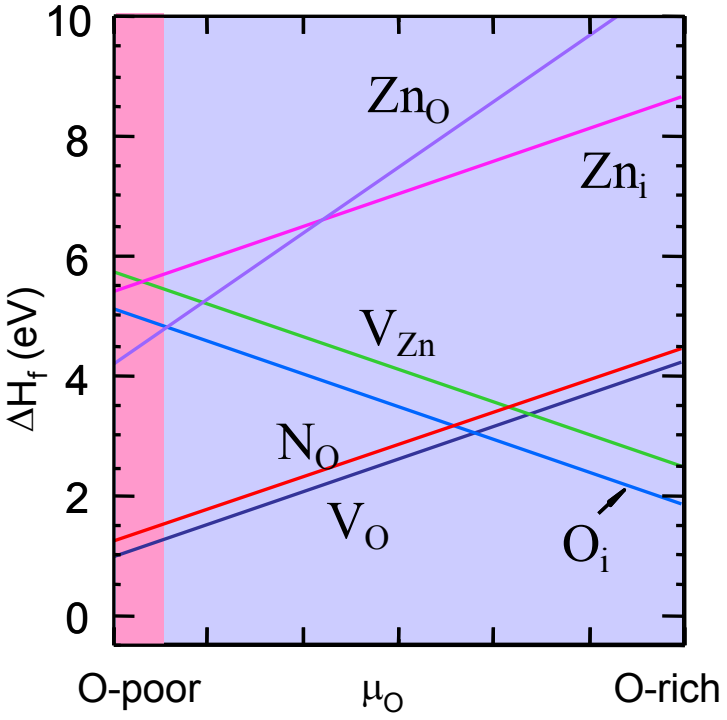
Origin of the p-type doping difficulty in ZnO

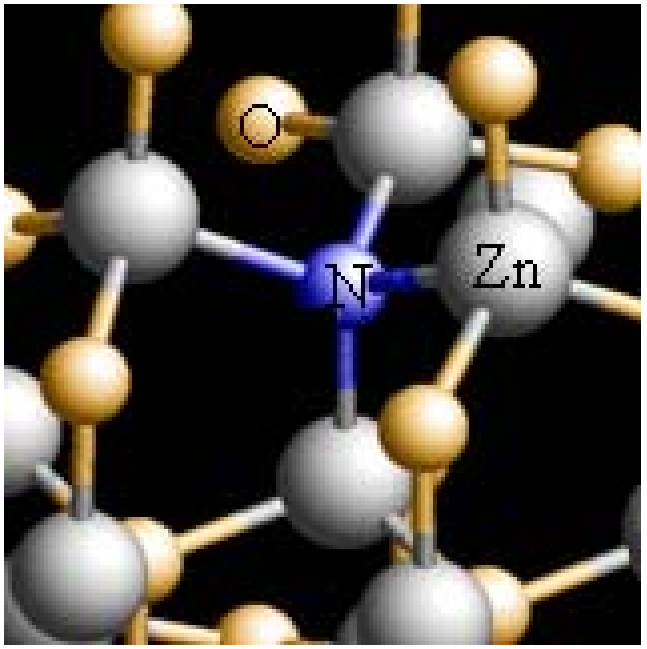
Main reasons of failure-to-dope

- The impurity atom has limited solubility in the host material, so not enough dopants are introduced
- The defect transition energy levels are too deep, so not enough charge carrier are generated at working temperature
- Spontaneous formation of opposite-charged "killer defects" (cation vacancy, anion vacancy, etc.), which pins the Fermi energy

S.-H. Wei, Computational Materials Science 30, 337 (2004)

Origin of p-type doping difficulty in ZnO: high acceptor formation energy





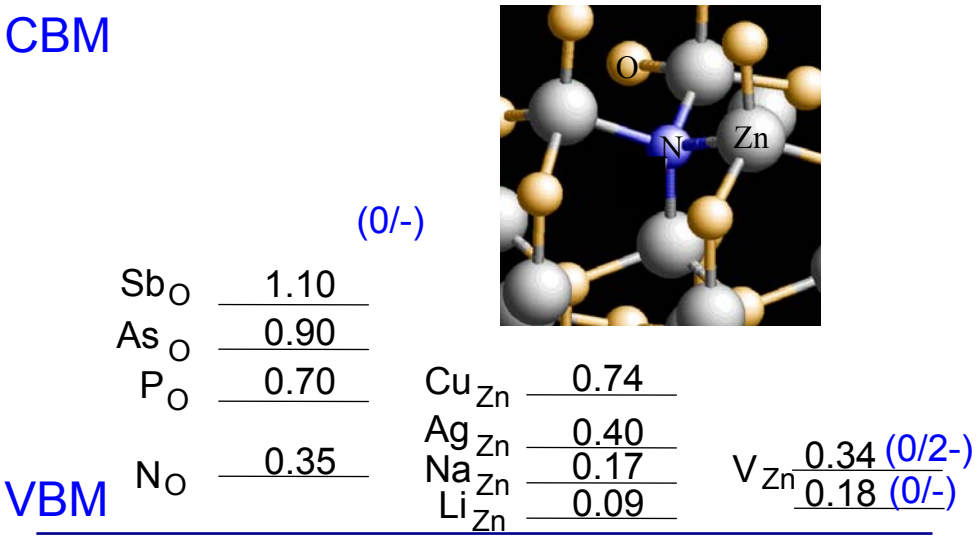
Due to the strong bonding and large formation energy of ZnO, intrinsic defect formation energies are large

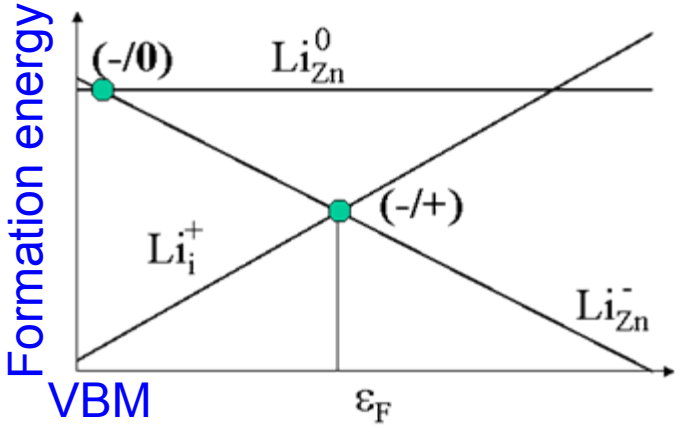
Calculate minimum defect formation energy of neutral N_O

$H_f(N_O)_{min}$ = 1.2 eV (N_2)

Origin of p-type doping difficulty in ZnO: high acceptor ionization energy

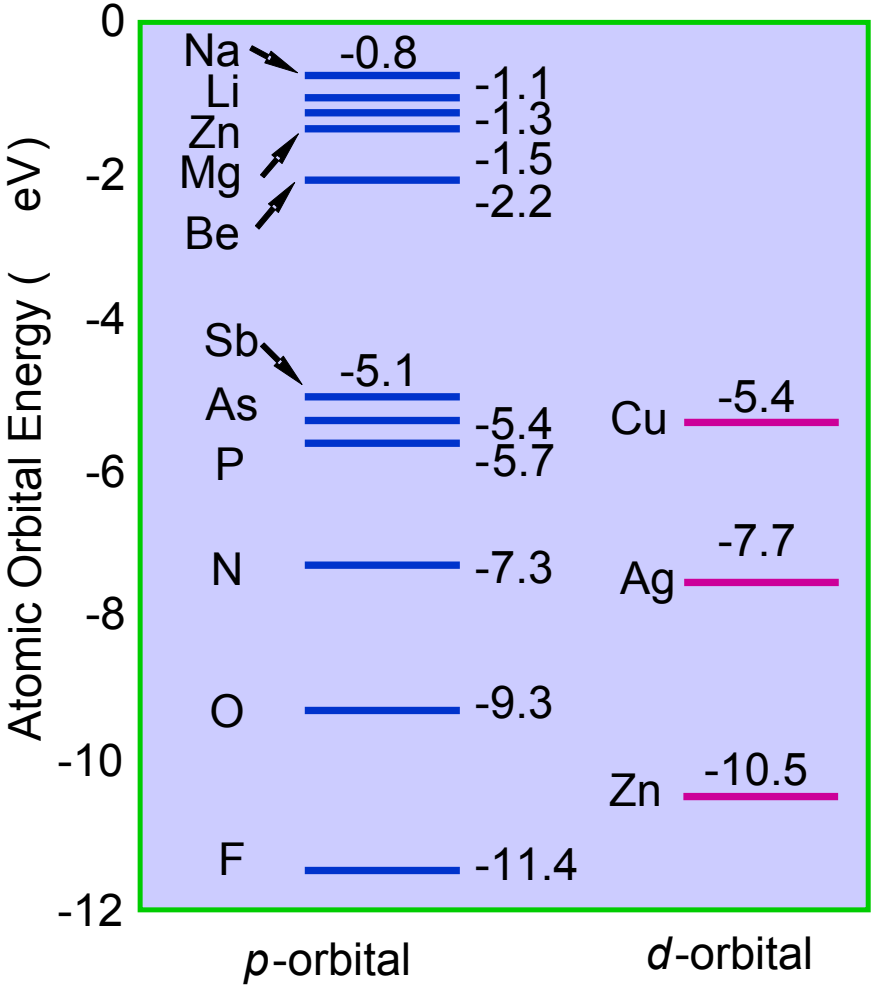
Acceptor energy levels in ZnO





- For group V on oxygen site acceptor, the lowest transition energy level N_O is 0.35 eV above the VBM
- For group IB on Zn site acceptor, the lowest transition energy level is also deep, at 0.40 eV for Ag_{Zn}
- Group IA on Zn site has relatively shallow defect level, but self compensation limits their use as effective acceptor

Origin of p-type doping difficulty in ZnO: high acceptor ionization energy



- An acceptor level above VBM has a wavefunction character similar to the VBM, i.e. it has an anion *p* and cation *d* orbital characters
- Oxygen *p* orbital energy is very low, there are no group-V elements that are more electronegative than O
- *p-d* coupling between host elements and dopants (e.g., N_O with Zn or Cu_{Zn} with O) is large

Strategies to overcome the doping limit

- Increase defect solubility by "defeating" bulk defect thermodynamics
- Reduce defect ionization level through proper codoping techniques
- Reduce defect compensation and ionization level by modifying the band edge states

Improve the Dopant Solubility by Adjusting Dopant Chemical Potentials

Increase defect solubility using non-equilibrium thermodynamics

- What controls the dopant solubility is the dopant chemical potential, μ_A. Therefore, the key to enhance the solubility of the dopant is to raise the chemical potential and avoid the formation of the precipitates of the dopants

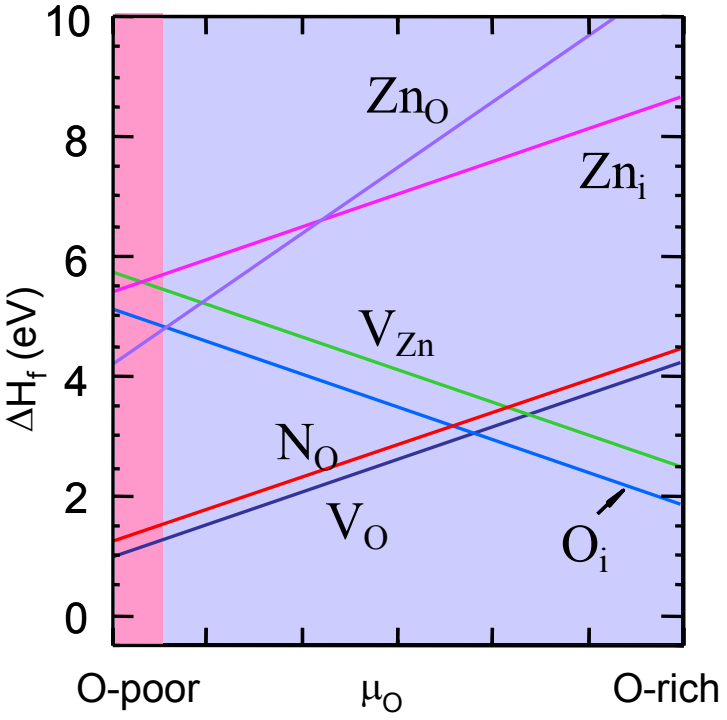
$$\Delta H^{(\alpha,q)}(E_F,\mu) = \Delta E^{(\alpha,q)}(E_F=0,\mu_i=0) + \Sigma\, n_i\mu_i + qE_F$$

- Choose the optimal host element chemical potentials
- Enhance solubility by metastable molecular doping
- Enhance solubility by epi-growth (e.g., MBE)

S.-H. Wei, Computational Materials Science 30, 337 (2004)

Choose the optimal host element chemical potentials

- The formation energy of N_O is the lowest under O-poor condition, whereas V_{Zn} is the lowest under the O-rich condition



$$\Delta H_f = E(ZnO:N) - E(ZnO) + \mu_O - \mu_N$$

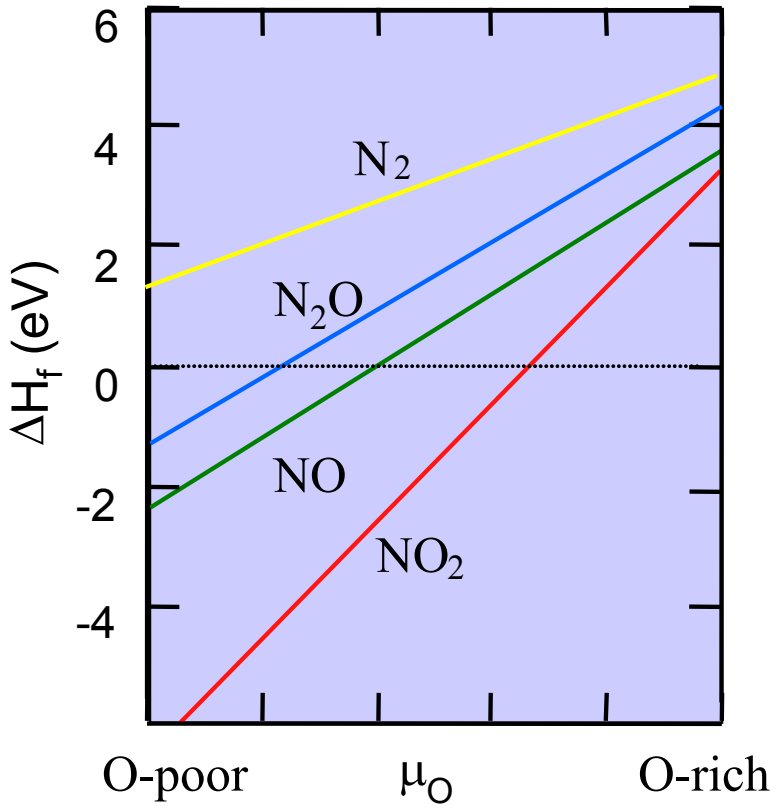
$$\Delta H_f = E(ZnO:V_{Zn}) - E(ZnO) + \mu_{Zn}$$

Enhanced solubility by molecular doping: ZnO:N

$$\Delta H_f = E(ZnO:N) - E(ZnO) + \mu_O - \mu_N$$

$$\Delta H_f = E(ZnO:N) - E(ZnO) + 2\mu_O - \mu_{NO}$$

$$\mu_N(N_2) < \mu_N(N_2O) < \mu_N(NO) < \mu_N(NO_2)$$



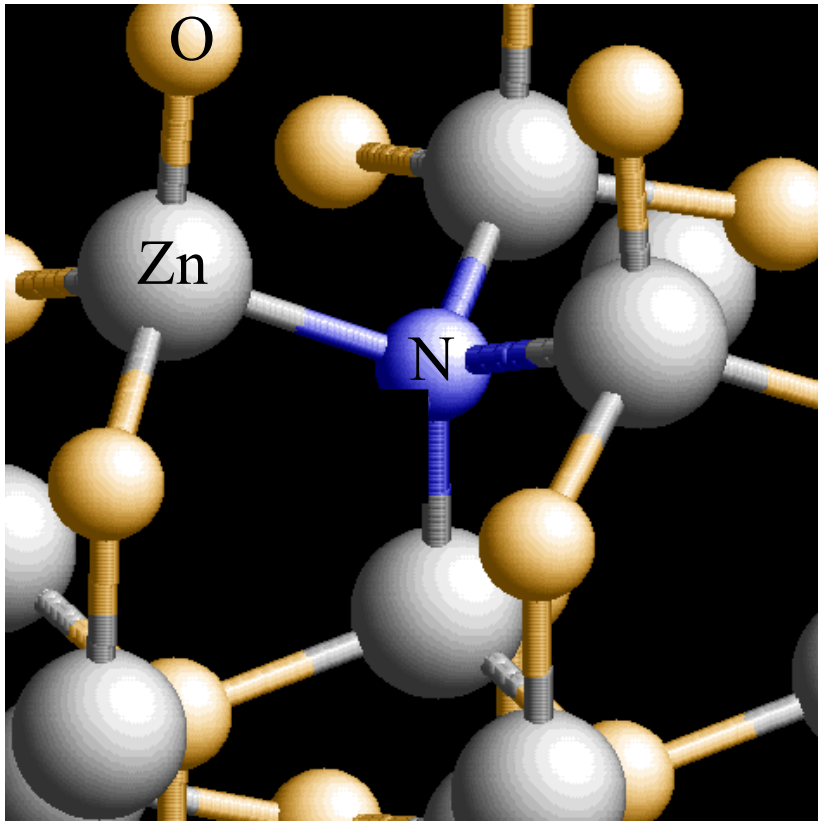
N chemical potential depends on the doping sources (N_2, N_2O, NO, NO_2)

N solubility in ZnO is much higher if NO or NO_2 is used as dopant

NO or NO_2 doping also avoids the formation of $(N_2)_O$, which is a compensation donor in ZnO

Yan et al., Phys. Rev. Lett. 86, 5723 ('01)

Single N atom in ZnO



Transition energy level of N_O

E(0/-) = VBM + 0.35 eV

Calculate minimum defect formation energy N_O

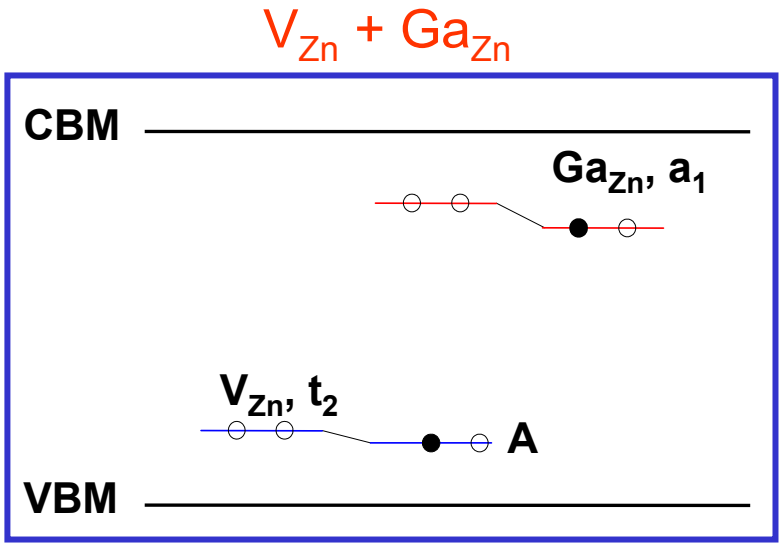
$H_f(N_O)_{min}$ = 1.2 eV (N_2)

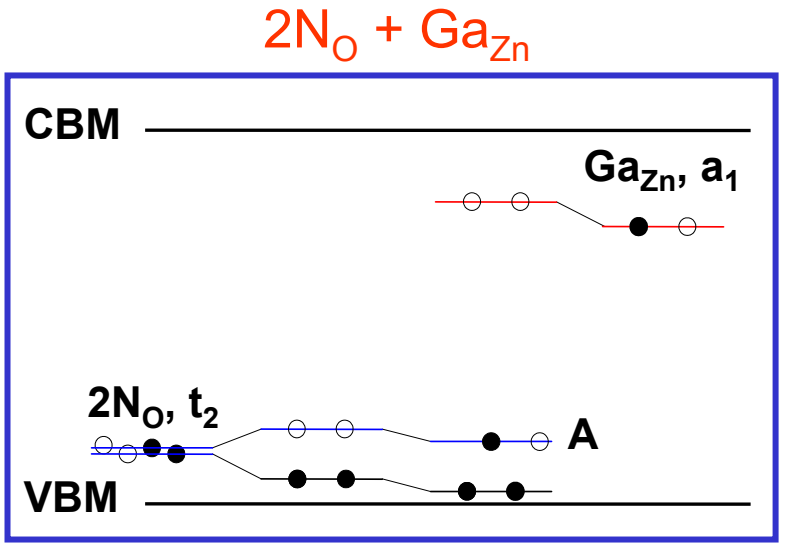
$H_f(N_O)_{min}$ = 0.4 eV (NO, Zn_3N_2)

Design shallow defect levels in ZnO using band structure calculation method

Effects of conventional co-doping

- Can co-doping lower the defect transition energy levels?

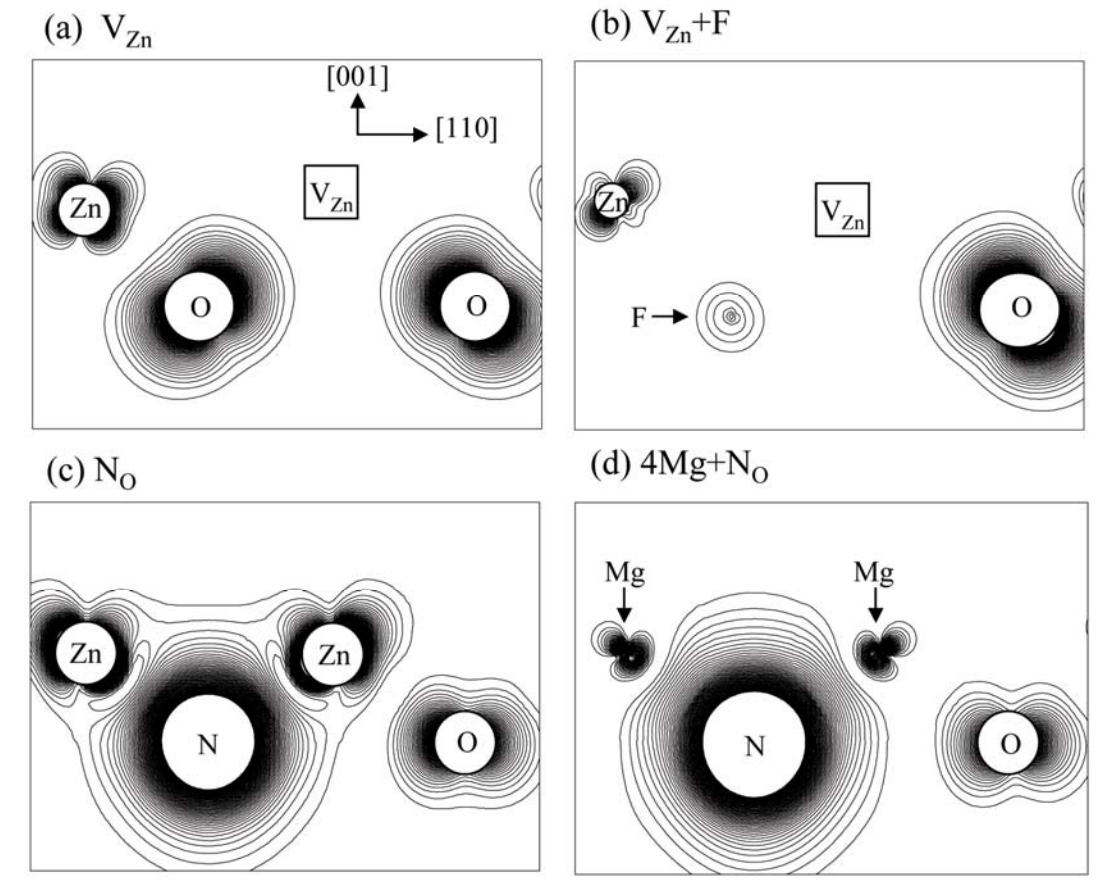


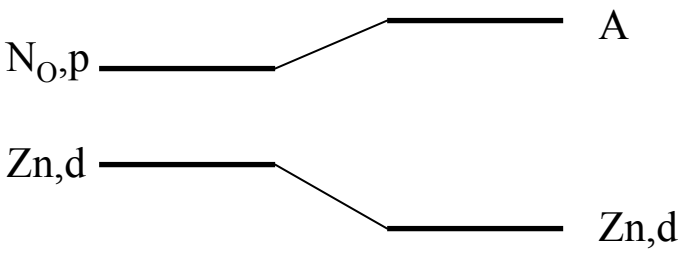


➢ The level repulsion effect is rather small because the donor state and the acceptor states have different symmetry

➢ The defect transition energy level may be lowered only if the defect complex consists a single donor and a single acceptor

Design shallow p-type dopants in ZnO





- Defect wavefunction has large weight on its neighboring atoms
- Replace O by the more electronegative F is expected to lower V_{Zn} energy level
- Remove p-d coupling between N_O and cation by replacing Zn with Mg or Be is also expected to reduce the acceptor energy level

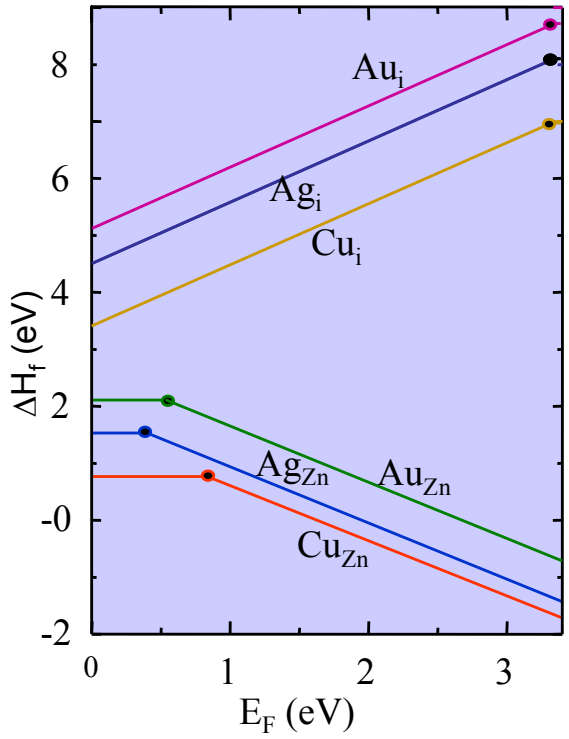
Design shallow p-type dopants in ZnO

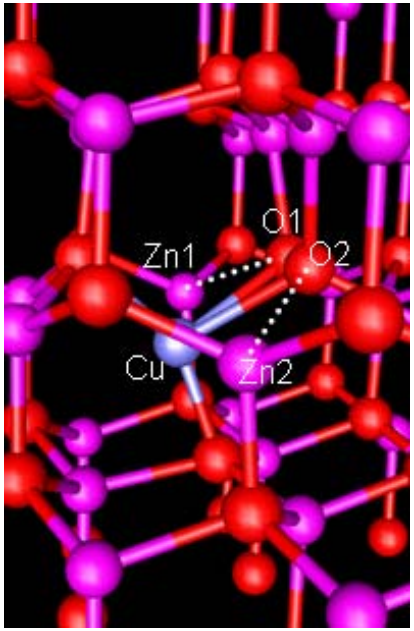
Defect	E_b	(0/-)	(-/2-)
N_O		0.31	—
N_O-Mg_{Zn}	0.3	0.29	—
N_O-$4Mg_{Zn}$	1.6	0.23	—
N_O-Be_{Zn}	0.1	0.22	—
N_O-$4Be_{Zn}$	1.9	0.12	—
V_{Zn}		0.18	0.34
V_{Zn}-F_O	−2.3	0.16	—

- The calculated defect ionization energy levels suggest that F and Be could be good p-type co-dopant for ZnO

[J. Li, S.-H. Wei, S.-S. Li, J. B. Xia, Phys. Rev. B **74**, 081201R (2006)]

Reduce self-compensation by introducing Group-IB acceptors in ZnO





- Cu_{Zn} has very deep acceptor level because of the large p-d coupling, but Ag_{Zn} has relatively shallower levels

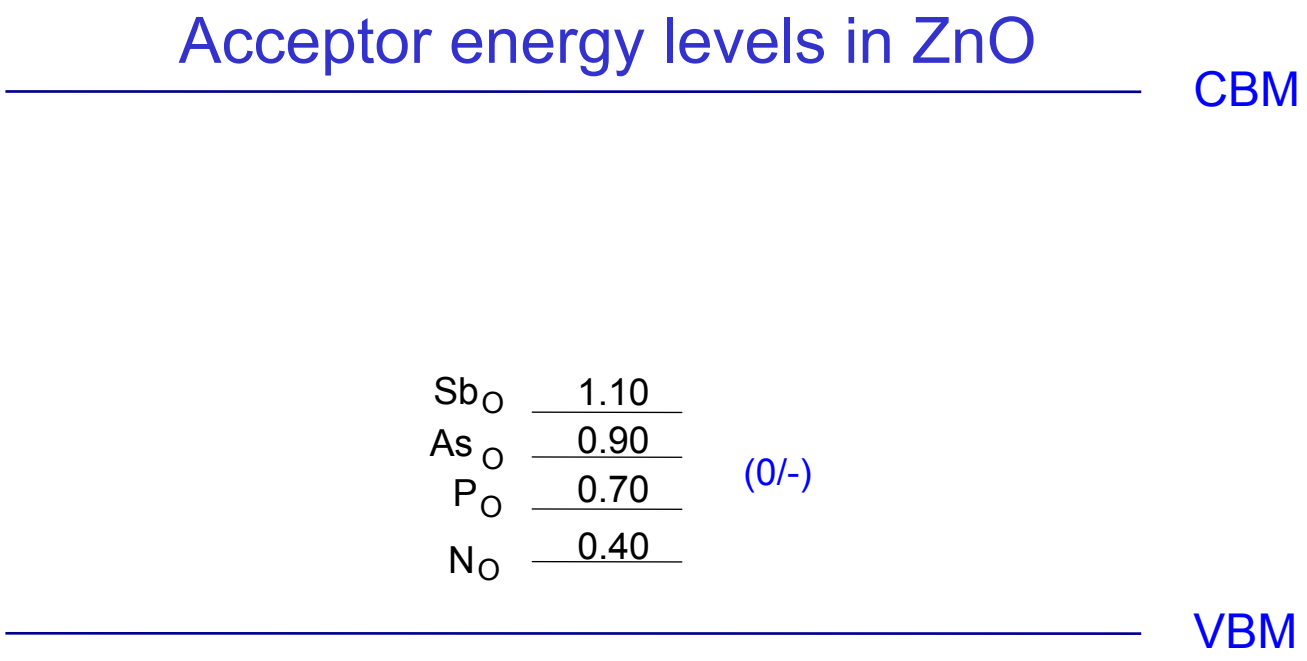
- IB_i is highly unstable, so self-compensation for IB dopants is low

Y. Yan, M. M. Al-Jassim, and S.-H. Wei, APL 89, 181912 (2006)

Large size mismatched p-type doping in ZnO:As

Background:

- p-type conductivity in As and P-doped ZnO have been observed and conventional doping model attributed the dopants to As_O and P_O
- We have show that As_O and P_O are unlikely to be the measured acceptor because
  - The formation energy is high (As and P is much larger than O)
  - The ionization energy of As_O and PO are very high ~ 0.8 eV



Large size mismatched p-type doping in ZnO:As

The new model:

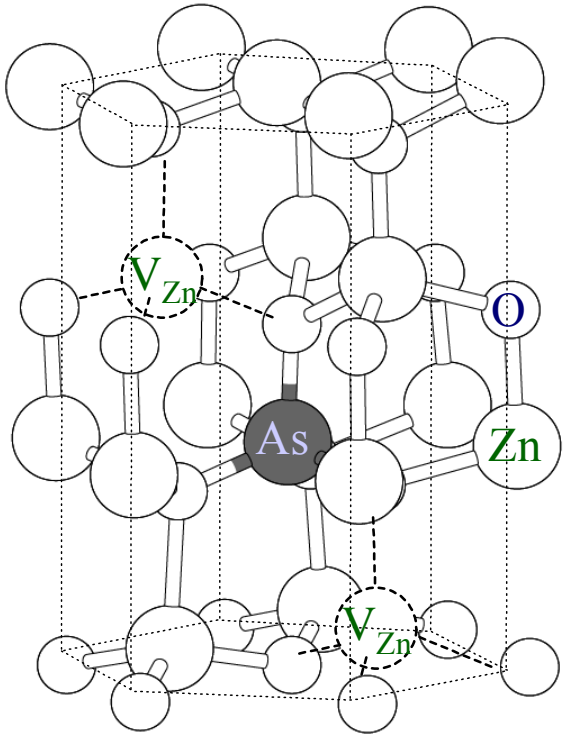
- Atomic size of As and Zn are similar

- As_{Zn} has relatively lower formation energy but it is a (triple) donor

- V_{Zn} is a native (double) acceptor with low formation energy

- One As_{Zn} and two V_{Zn} bind strongly and form a new acceptor complex (As_{Zn}-$2V_{Zn}$)

- The complex has low formation energy and low ionization energy (~ 150 meV)

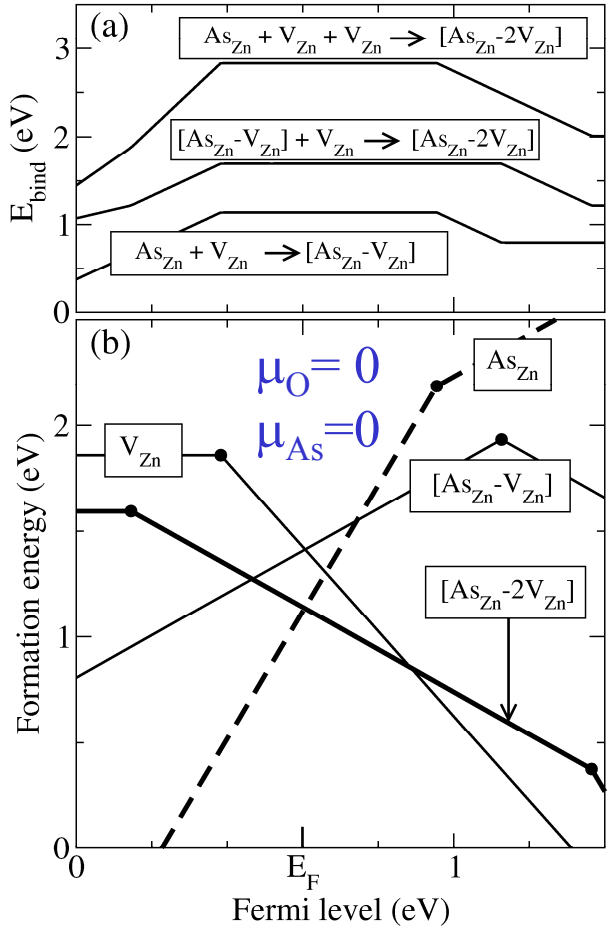


[As_{Zn}-$2V_{Zn}$ complex]

*Limpijumnong, Zhang, Wei, and Park PRL **92**, 155504 (2004).*

Large size mismatched p-type doping in ZnO:As

Calculated binding energy and defect formation energy for various As-related defect complexes in ZnO

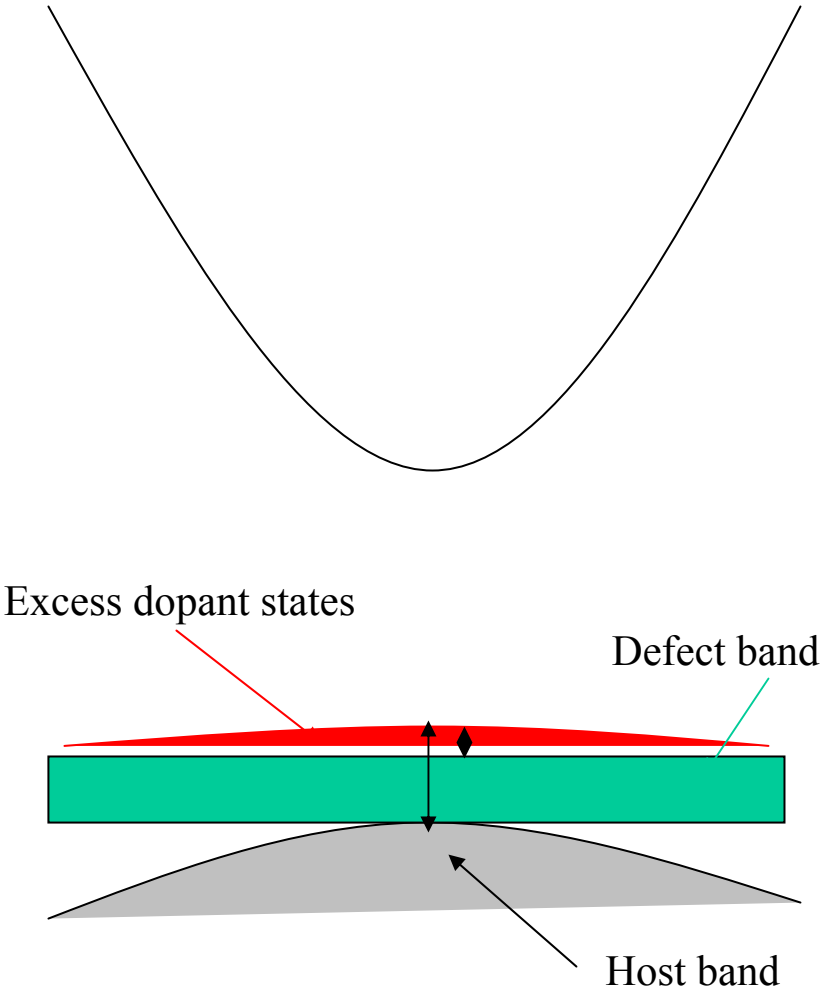


- Strong Coulomb interaction and strain compensation lowers the formation energy of the As_{Zn}-$2V_{Zn}$ defect complex

- Coupling between the As_{Zn} donor states and the V_{Zn} acceptor states lowers the ionization energy of the complex relative to V_{Zn}

Modify the host band structure to reduce ionization energy and compensation

Universal approach to overcome the doping asymmetry in wide-band-gap semiconductors

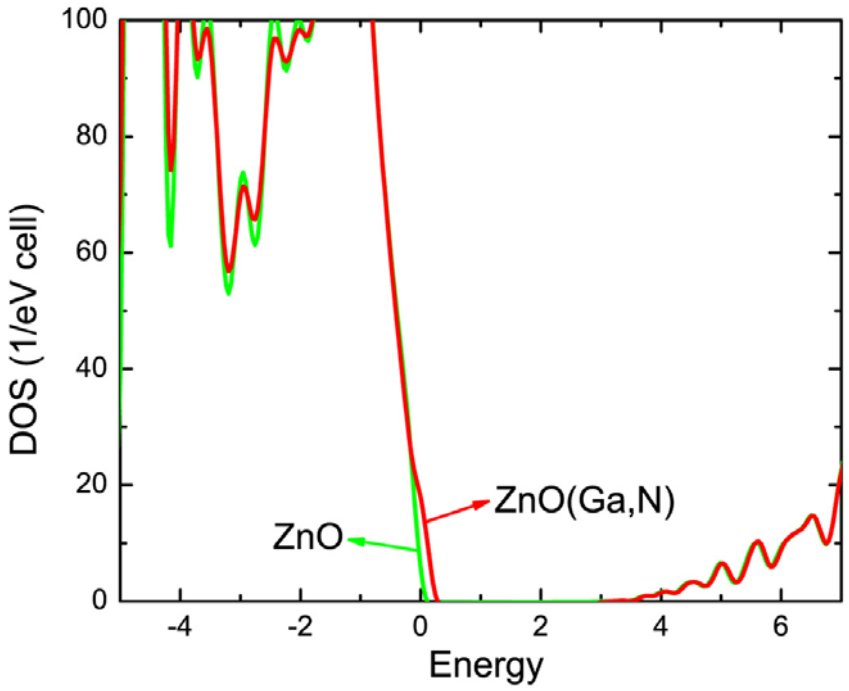


- First, through effective doping of mutually passivated defect pairs, we introduce a fully compensated defect band near the VBM or CBM of the host

- Second, after the fully compensated insulating phase is formed, use excess dopants to dope the passsivated system by ionizing the defect band

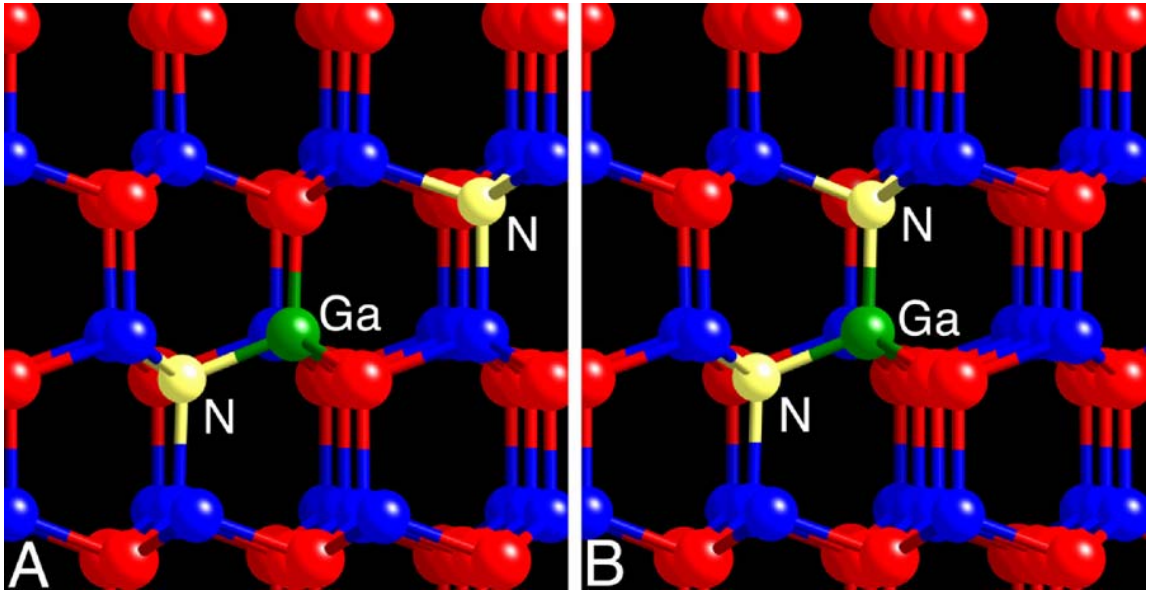
Y. F. Yan, et al., Phys. Rev. Lett. **98**, 135506 (2004)

Modify the valence band edge of ZnO by passivate doping of Ga with N



➢ N combined with Ga creates a passivated defect band above the host ZnO VBM

Create shallow acceptor level by doping the passivated ZnO:(Ga+N) system using excess N



- The calculated defect level of N is about 0.1 – 0.2 eV above the defect band

[Y. Yan, J. Li, S.-H. Wei, M. M. Al-Jassim, Phys. Rev. Lett. **98**, 135506 (2007)]

Possible dopants or dopant complexes for p-type doping in ZnO

- Based on defect wavefunction analysis, various microscopic models have been proposed to reduce the ionization energy of acceptor level in ZnO

Ag_{Zn} ; $V_{Zn} + F_O$

$Mg_{Zn} + N_O$; $Be_{Zn} + N_O$

$As_{Zn} + 2V_{Zn}$; $P_{Zn} + 2V_{Zn}$

- Doping of defect band is an effective and universal approach to doped wide band gap materials such as ZnO

$N_O + (N_O + Ga_{Zn})_{\text{defect band}}$

Summary

We have analyzed the origin of p-type doping difficulty in ZnO. Several strategies have been proposed to overcome the doping difficulty

- Increase defect solubility by "defeating" bulk defect thermodynamics using
  - optimized host elements chemical potential
  - surface enhanced defect solubility
  - molecular doping
  - large size-mismatched antisite doping

- Reduce defect ionization level by
  - combining donor with acceptor to modify defect wavefunctions
  - reducing p-d coupling between defect level and host states

- Design new dopable materials by adjusting the band edges states using passivated doping and subsequent doping using the same dopants

Thank You for Your Attention !